Literature Survey on the Chemistry of Macromolecules

- Historical Back Ground

Macromolecular science was born in the middle of the last century and made a rapid progress in last several decades to fill the gap between traditional disciplines and to meet the practical needs of the new era. However, the macromolecular science is not a mere extension of chemistry or physics but stands at the crossroads of chemistry, physics, and life science. Especially, the macromolecular science has been regarded as an important field of science for understanding of biological phenomena at a molecular level. Macromolecules are known as a typical complex system and have recently attracted the great interest of many scientists in the field of chemistry and physics.

Before 1960 little work had been reported concerning the coordination chemistry of macrocyclic ligands. Since the early 1960s, the synthesis of a very large number of metallated heterocycles had been reported(1).

These synthetic endeavors had provided the raw material for a multitude of research projects in many areas including biological studies, metal-ion catalysis, and metal-ion discrimination. Some of these studies have resulted in industrial and medical applications(2). The macro molecules such as natural heme proteins, chlorophyll and vitamin B_{12}, reveal distinctive coordination chemistry and biological importance of complexes with macrocyclic ligand(3).

Supramolecular chemistry is a novel area of multi disciplinary chemical research that developed during the past few decades. It focuses on complex structures formed by the association (covalent or not) of several moieties and on the novel chemical properties resulting from this higher complexity. Supramolecular chemistry has two facts; one based upon the synthesis of complex organic structures by synthetic chemistry, and one in which the structural complexity is achieved by self-assembly and self-organization of smaller units without the help of covalent bonds.

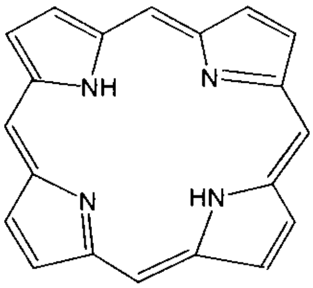
One of the major features of macrocyclic complexes is their remarkable thermodynamic stabilities and resistance to demetallation. Thus the macrocycle can be regarded as a protecting group for the metal ion, enabling unusual reactivity at other coordination.

Macrocycles are cyclic organic ligands which incorporate hetero atoms which may bind to transition metal and other guest ions within the ring. Several macrocycles occur in nature and perform important biological processes, e.g. heme proteins, cytochromes, vitamin B_{12}. Synthetic macrocyclic ligands incorporating O, N and S donor atoms have useful for applications including selective sites and/or stabilisation of unusual metal fragments oxidation states. There are different types of macrocycles involving phosphine, arsine, selenoether or telluroether functions, which are much less well known than amine or thioether macrocycles.

Macrocyclic ligand

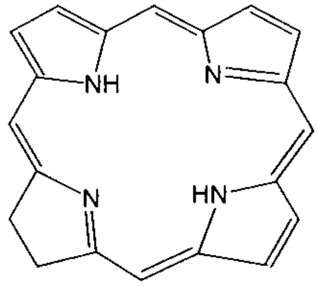
Monocyclic or polycyclic ligands with metal ligating groups incorporated into or attached to a cyclic back bone containing 9 or more atoms which contain at least 3 metal ligating groups. Examples for macro cyclic ligands are:

1- Macrocyclic ligand have biological importance such as porphyin (I) and chlorin (2,3-dihydro porphyin) (II).



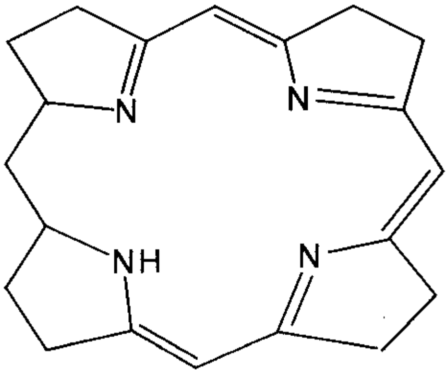
Porphin

(I)



Chlorin
2,3-DihydroProphin
(II)

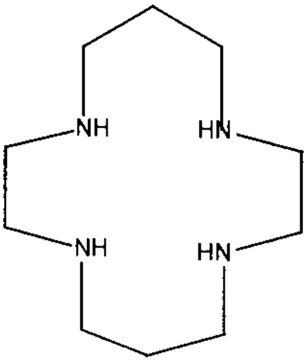
2- Some macrocyclic ligand present in nature such as chlorophylls contain Mg^{2+}bound to a substituted chlorine system, protein, vitamin B_{12} contains Co^{3+} bound to a corrin ring system (III), hemes found in hemoglobin, cytochromes, catalase and peroxidase.



Corrin

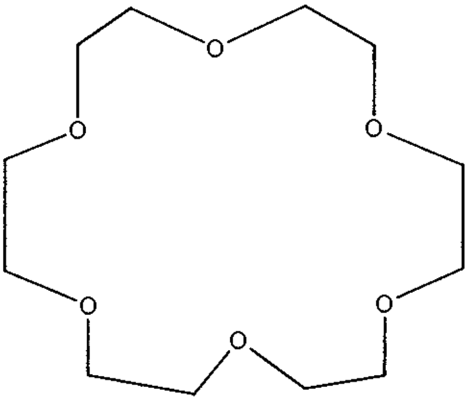
(III)

3- Macrocyclic ligands containing mainly N, P, S as donor atoms prefer to bind to transition metals such as porphyrin and cyclam (IV).



Cyclam
(IV)

4- Macrocycles containing mainly O donor atoms prefer to bind to alkali metals and alkaline earths, for example; ligands include the crown ethers (V).



18-Crown - 6
(V)

Preparation of macrocyclic complexes

A major portion of inorganic chemistry may be called coordination chemistry, that is the investigation of the properties, structure, and reactions of complexes formed by ligands coordinated to a transition metal center. Complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated into a cyclic ligand that surrounds the metal ion, commonly referred to as a macrocyclic ligand. The fact that some macrocyclic ligands can be made only in poor yields, or not at all, in the absence of metal ions has lead to the concept of the (template effect), i.e., that the metal coordinates and properly arranges the ligand precursor fragments in its coordination sphere, there by assisting the linking process that produces the macrocyclic ligand.

Spontaneous self-assembly reactions hold a fascination for chemists as we attempt to mimic anabolic reactions without enzymes, and synthesize new tailored polymers with special electrical properties. The ability of certain transition metals, especially nickel, to coerce intramolecular Schiff-bases reactions into macrocycle formation is well known(4).

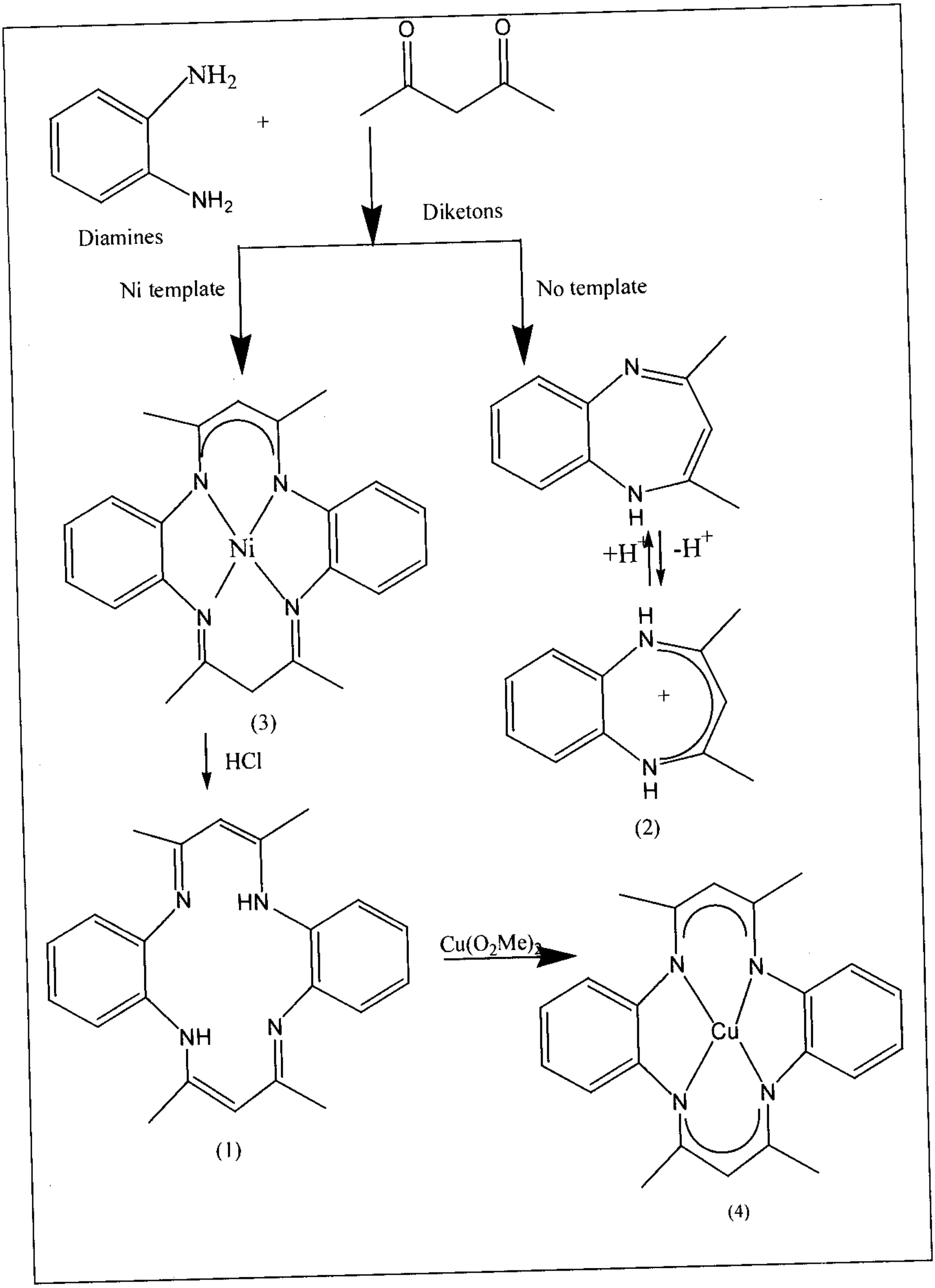
The macrocyclic complexes product can give low yields with poor solubilities, involve difficult product separations, long reaction times, or require hazardous perchlorate counteranions. The preparation described below is intended to overcome these difficulties and yield a variety of macrocyclic complexes.

Of the many (macrocycle template) reactions available, the preparation of Geode's macrocycle. Scheme (1) is particularly attractive, for the low-cost of the starting materials, and the good solubility/ crystallinity of most of its complexes.

Preparation of (compound 3) (Ni (Mac)) from the condensation of 1,2-diaminobenzene (16.0 mmol), dry butanol (30 ml), and acetylacetone (17 mmol) added by syringe. The flask was set up in an oil bath on a hot plate stirrer (alternatively a heating mantle may be used instead, but a few boiling chips must be added) and equipped with a reflux condenser. The mixture was brought to a brisk reflux and stirred under reflux for 3h.

Methanol was added and the mixture was cooled in an ice-salt bath at least 15 min to precipitate the non-polar macrocyclic complex. The mixture was filtered and recrystallized by methanol. The nickel complex was suspended in absolute ethanol and a moderate stream of HCl gas was bubbled through the suspension, agating occasionally for 10-20 min, $[H_4(Mac)] [NiCl_4]$ was formed.

Preparation of (compound 4) from the reaction of $Cu(O_2CMe)_2$ .H2O and methyl cyanide (40 ml) in a fume hood. The flask was equipped with a condenser and refluxed until all of the copper acetate had dissolved. A suspension of the (macrocycle 3) in methyl cyanide containing triethylamine was added to the reflux condenser and residual macrocycle washed with methyl cyanide and air dried to obtain the product.



Scheme (1): Types of preparation of macrocyclic complexes.

- Literature Survey:

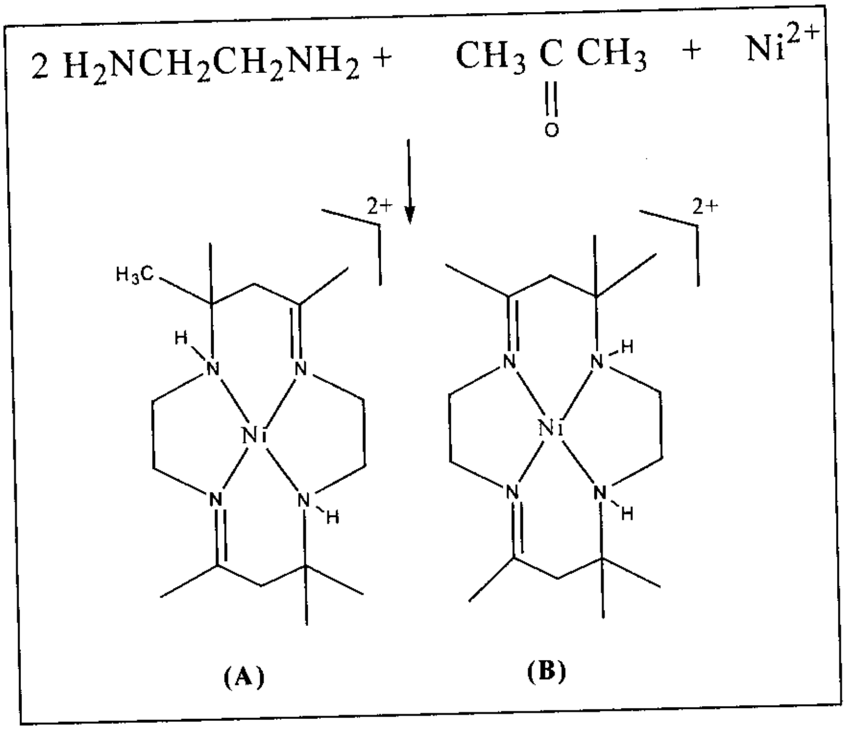
Tetraza[14]annulene nickel (II) macrocyclic complex obtained by template condensation of 1,2-phenylenediamine with 2,4-pentanedione in the presence of nickel(II) ion was described by Ger(5). Tetraaza[14]annulene metal complexes have a number of structural features in common with the porphyrins and the complexes have also received much attention as catalysts.

However, most macrocyclic complexes formed by template condensation of 1:1 mixture of two molecules of diamines such 1,2-phenylenediamine, ethylenediamine and propylenediamine with two molecules of diketone such 2,4-pentanedione were symmetrically.

The 7,16-positions of tetraaza[14]annulene nickel(II) complex had been found to be a reactive nucleophilic center which was named methane site. Macrocyclic complexes are typically very stable species and this can give rise to unusual structural, electronic and/or electrochemical properties. There are now many complexes incorporating N, O or S donor atoms. The synthesis of macrocyclic and polydentate ligands incorporating specific donor sets and arrangements, studying the coordination chemistry of these ligands with transition metal ions and probing the redox properties and reactivity of the resultant complexes with molecular substrates(5).

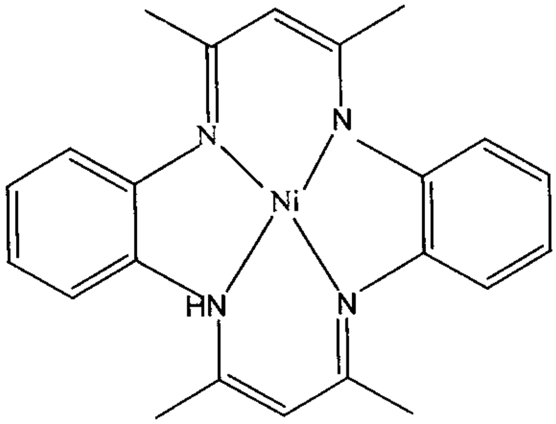
Polyaza macrocyclic ligands with alkyl pendant arms at the donor nitrogen atoms and their metal complexes have received much attention because of their structural and chemical properties, which are often quite differ from those for the unalkylated macrocyclic compounds. Although various per-N-alkylated tetraazamacrocyclic compounds had been prepared by alkylations on the secondary nitrogen of performed macrocycles, examples of partial-N-alkylation macrocyclic ligands are relatively rare. Moreover, those with more bulky alkyl groups than methyl are even rare. This may be arises from the fact that the selective alkylation is more complicated and requires several steps. Therefore, in the direct synthesis of free macrocyclic ligands in which bulky alkyls are partially substituted on the donor nitrogen was studied (6). Although some unsaturated macrocycles have been obtained by non template reactions of α, β-unsaturated ketons with diamines, most of the ligands had no constituent at the nitrogen atoms.

One of the earliest examples of a templated reaction involved the reaction of ethylenediamine (en), $H_2NCH_2CH_2NH_2$, with acetone in the presence of nickel(II) ion(7) . The products of this reaction A and B were remarkable in their stability under conditions that would destroy many other nickel(II) compounds, i.e., strongly acidic, oxidizing and reducing conditions. Both A and B were formed; however, the amount of B is small and its greater solubility allows for the isolation of pure A.


$$2\,H_2NCH_2CH_2NH_2 + CH_3\underset{\underset{O}{\|}}{C}CH_3 + Ni^{2+}$$

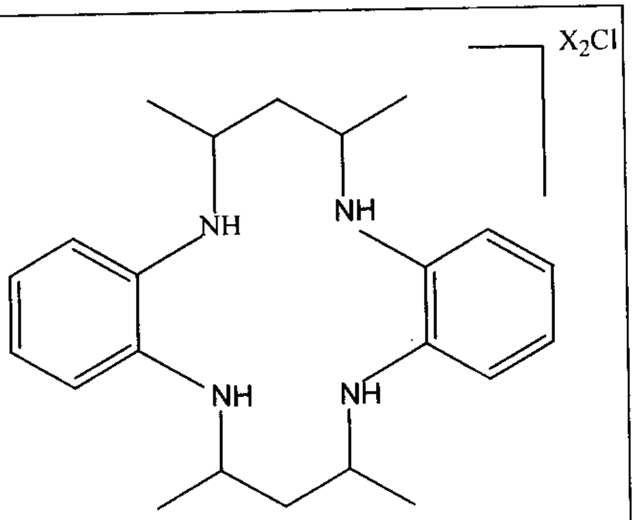
(A) (B)

5,7,8,14-tetramethyldibenzo(b,i)-1,4,8,11tetraazacyclotetradecane nickel(II)chloride in (VI-VII). (Ni($Me_4B_2O_2$(14)aneN_4))Cl_2)(VI) was obtained as orange red salt by Fe/HCl reduction of the corresponding tetraaza annulene complex (Ni($Me_4B_2O_2$taa)). The cyclam derivatives exhibited very rich coordination chemistry with a variety of transition metal ions (8). The dibenzo cyclam macrocycles could prove to be a better candidate for development of Ni(II) selective electrodes. The γ-carbon atoms in MR_4taa complexes posses remarkable nucleophilicity(9), which can be exploited for binding a variety of groups in order to build molecular super-structures and supramolecular assemblies(10).



(VI)

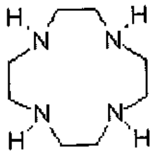
(Ni(Me_4BzO_2 taa))



(VII)

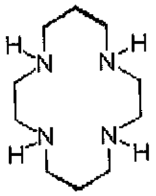
(Ni(Me_4BzO_2(14) ane N_4))Cl_2

The macrocycles cyclen(VIII) and cyclam(IX) had been known for several decades, and their complexation chemistry with a large variety of metal ions has been studied thoroughly(11). Such macrocyclic ligands often lead to complexes with enhanced thermodynamic and kinetic stability with respect to metal ion dissociation, compared to their open-chain analogues.



"cyclen"

VIII

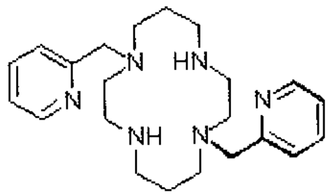


"cyclam"

IX

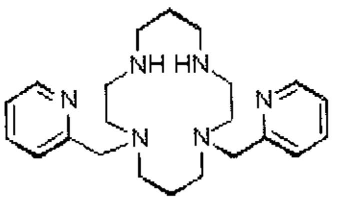
Metal ions with a preference for coordination numbers > 4 will require further ligands to be bound (apart from the four nitrogen atoms of the macrocycle), and these may be provided by the functionalisation of the macrocycle with additional pendent coordinating groups. This leads to higher-dentate ligands whose properties and selectivity for certain metal ions over others may be quite different from those of the unsubstituted parent macrocycles.

Cyclam-based macrocycles having two additional coordinating groups (e.g. pyridyl groups) had been prepared (12) via di-N-alkylation. Since cyclam has C_2 symmetry, there are three different isomers for a di-N-substituted system, the 1,4-, 1,8- and 1,11-functionalised ligands. The effect of this isomerism on the structures of the complexes formed with various transition metal ions was investigated. For example, 1,8- and 1,11-bis(pyridylmethyl) cyclam(X) was synthesized, and it turned out that the structures of the complexes they form with copper(II) are completely different.



1,8-bis(pyridylmethyl)cyclam

(X)

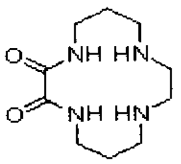


1,11-bis(pyridylmethyl)cyclam

(XI)

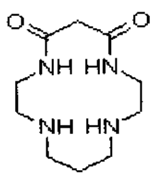
The nickel (II) complexes were also different. For example, whilst the copper complex of the 1,8-ligand has pyridine groups occupying the axial positions with the four nitrogens of the macrocycle in the orthogonal plane, nickel formed a very different complex, in which the pyridine groups coordinate in mutually cis positions(12).

In some closely related work, the chemistry and complexation properties of macrocyclic dioxotetraamines (XII-XIV) were investigated(3). These macrocycles contain two amino nitrogens and two amides, for example the three macroycles below, which were referred to as gem-, cis- and trans-dioxocyclam.



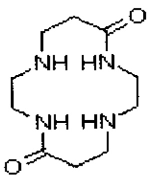
gem-

(XII)



cis-

(XIII)



trans-

(XIV)

The amino nitrogen was alkylated with additional coordinating groups to obtain new hexadentate ligands. They were able to bind to metals like copper (II) and nickel (II) with simultaneous dissociation of the two amide protons, such that metal binding was highly pH-sensitive and reversible (a very useful property for metal-sensing applications). Copper(II) complex of a functionalized trans system at neutral and basic pH was crystallized, and found very different structures according to whether just one or both of the amides are deprotonated.

Synthesis of macrocyclic dioxotetraamines, typically, the 14-membered tetraamine macrocycles cyclam, monooxocyclam and dioxocyclam like porphyrins and corrin were discussed (1). Incorporate metal ions in to their cavities to form stable complexes macrocyclic dioxotetraamines are unique oxidation states of some transition metals. These properties have been applied to super oxide dismutase-like catalysts.

The two-amido groups in macrocyclic dioxotetraamines are equivalent, when coordinated to a 3*d* metal ion, they will be deprotonated simultaneously. As for dioxotetraamines, the presence of a non-deprotonated or singly deprotonated complex is unlikely.

The first and most extensively studied series of synthetic tetraaza macrocycles were initially prepared by Curtis(13), who reported that the reaction of tris-(1,2-diaminoethane)nickel(II) perchlorate and acetone at room temperature produced a yellow crystalline product.

The Tris(2-aminoethyl)amine copper complex with 4-dimethyl aminopyridine, $[Cu(tren)(DMP)](ClO_4)_2CH_3CN$ (where tren is(tris(2-aminoethyl)amino, DMP is 4-dimethylaminopyridine), had been synthesized and characterized by elemental analysis, conductivity measurement, thermal analysis, magnetic measurement, electronic, IR and ESR spectral studied(14). The X-ray crystal structure revealed that the copper(II) ion is in a distorted triagonal bipyramidal geometry with the three primary amine groups of the tren ligand forming the equatorial plane and the tertiary amine and the 4-dimethylaminopyridine molecule on the apical positions.

Mixed ligand Ni(II) complexes of compositions $[Ni(py)_2(ttcH)(H_2O)$ (1), $[Ni(NH_3)(ttcH)(H_2O)_2$ (2), $[Ni(daet)(ttcH)(H_2O)_2$ (3), $[Ni(dpk)(ttcH)(H_2O)$ (4) and $[Ni(hexac)(ttcH](H_2O)$ (5), (py = pyridine, daet = 1,2-dianilinoethane, dpk = di-2-pyridyl ketone, hexac =1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane, $ttcH_3$ = trithiocyanuric acid), had been prepared and characterized by means of elemental analysis, IR and UV-VIS spectroscopy and magneto chemical measurements(15). Magnetic properties of $Ni(NH_3)(ttcH)(H_2O)_2$ were studied from 82-298 K. The complexes (1-4) were probably penta coordinated.

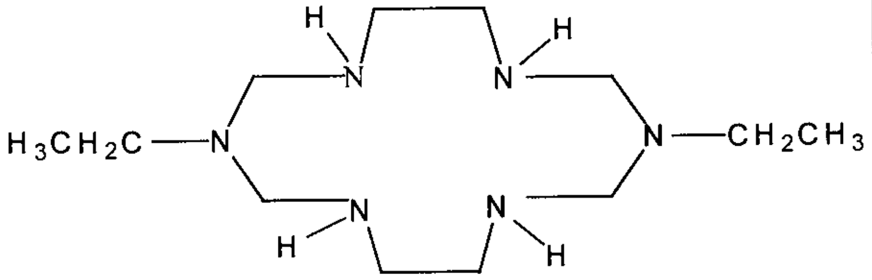


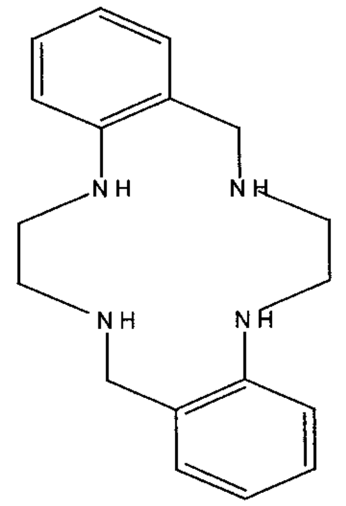
Figure: Hexaaza macrocyclic ligand hexac (1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane)

(XV)

New synthetic methods for the preparation of macrocyclic amido-N donor ligands were provided by Wylie (16). The primary method of the invention involved, in general, only two synthetic steps. In the first step, an, alpha, or, beta, amino carboxylic acid was allowed to react with an optimal (approximately stoichiometric) amount of an activated malonate or oxalate derivatives with mild heating. Upon completion of the double coupling reaction, hydrolysis of the reaction mixture yielded a diamide containing intermediate (a macro linker). In the second step, stoichiometric amounts of a diamine, preferably an o-phenylenediamine, were added to the macro linker intermediate in the presence of a coupling agent and heat. This second double coupling reaction was allowed to proceed for a period of time sufficient to produce a macrocyclic tetraamido compound. The constituent groups on the alpha or beta amino carboxylic acid, the malonate and the aryl diamine might all be selectively varied so that the resulting tetraamido macrocycle can be tailored to specific desired end uses. The macrocyclic tetraamide ligand may then be complexed with metal, such as a transition metal, and preferably the middle and later transition metals, to form a robust chelate complex suitable for catalyzing oxidation reactions.

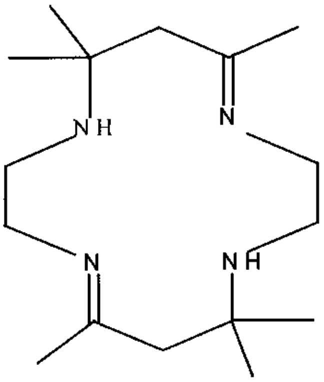
Synthesis of macrocyclic complexes for Cu(II),Co(II) and Ni(II) complexes of varies macrocyclic ligands had been synthesized in high yields by the template condensation reactions of amines and formaldehyde in presence of metal ion(17). The electronic spectra, redox properties and M-N bond distances of the complexes were found to depend on the structure of the macrocycle. Especially the sub ring moieties fused to the main 14-membered macrocyclic frame work and the alkyl groups attached to the coordinating nitrogen donors affected such properties predominantly. Some Ni (II) complexes exhibit equilibrium between square planar and octahedral species in the coordinating solvent. There was a qualitative correspondence between the ligand field strength, and the M-N bond distance in the macrocyclic complexes. As the ligand field strength decreases, the reduction potential and M-N bond distance increased.

Synthesis of the 14-membered macrocyclic trans-N_4 dibenzo ligand (XVI) with Cu(II) complexes have saddle-shaped structures with short intramolecular hydrogen bonds with a more or less planar arrangement of the four N donor atoms. A similar conformation is seen in Zn(II) and Pb(II) complexes(18). The metal atom is incorporated with in the macrocyclic cavity with rather short metal-to-nitrogen bond lengths. In all of the complexes, the metal-to-ligand distances originating at the nitrogen atoms in β-position (with respect to the aromatic ring) were significantly shorter than the donor bonds of the (phenylene) N atoms.



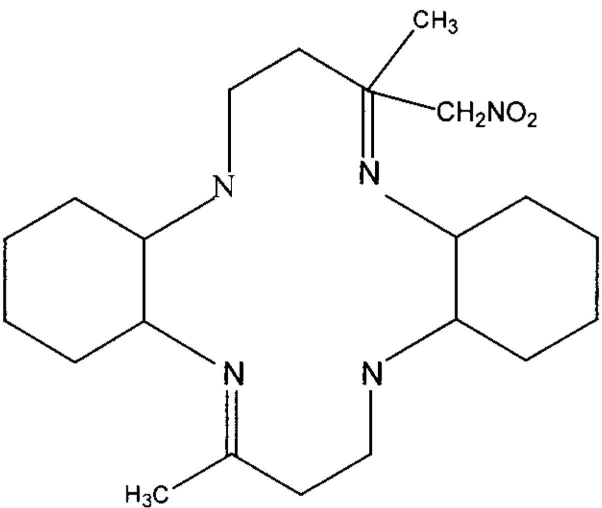
(XVI)

Hay et al (19) prepared the copper (II) complex of the β-amino ketone (XVII). In basic solution the complex showed base-catalyzed ring closure to give the copper(II) complex of trans macrocyclic. This ring closure occurred by intermolecular reaction involving the hydroxo complex [Cu(II)OH]$^+$.



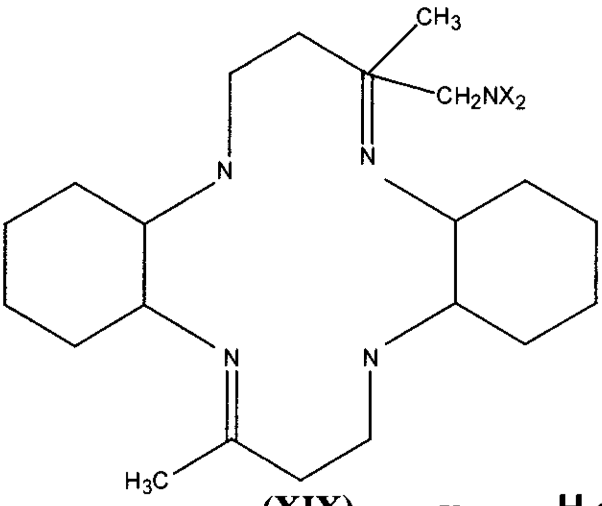
(XVII)

The square planar copper complex (3,14-dimethyl-3- nitromethyl-2,6,13,17-tetraaztricyclo [16.4.0.0/(7.12)] dococa-13-ene) containing one C-nitro methyl pendant arm was synthesized by the nucleophilic addition of deprotonated nitro methane to the diimine complex(20).



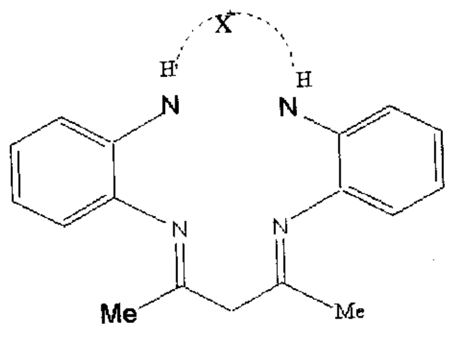
(XVIII)

The copper(II) complex in (XVIII) was relatively stable against the dissociation of the nitro methyl group even in basic acetonitrile solutions, in contrast to the corresponding nickel(II) complex. Reduction of the nitro group of (M-XVIII)$^{2+}$ (M=Ni(II) or Cu(II)) produced the square- pyramidal complex (Cu(XIX))$^{2+}$or octahedral complex for (Ni(XIX)(H2O)$^{2+}$ containing one C-amino ethyl group, which is coordinated to metal ion.



(XIX) X ⟶ **H or O**

A new series of 13-14- memered tetraazamacrocycle complexes (M(XX))x_2 (M=Ni(I) and Cu(II) , x = Cl or NO_3) had been synthesized(21) by template condensation reaction of o-bromo aniline , 2,4-pentanedione and primary diamines in methanol. A square planar geometry was proposed for the nickel and copper complexes. The complexes were characterized by IR, ^{1}HNMR, ESR, electronic spectra, conductivity and magnetic susceptibility.

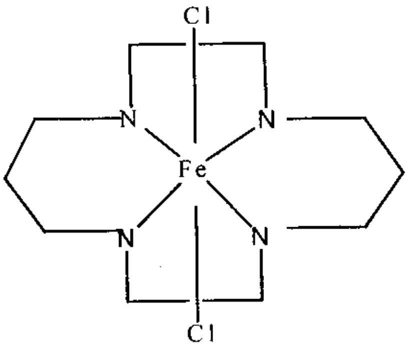


(XX)

The tetra methyl dibenzocyclam derivative was synthesized from condensation of acetylacetone and o-phenylenediamine with nickel acetate in butanol (22). The prepared compound was used for fabrication of potentiometric sensor for Ni(II) metal ion.

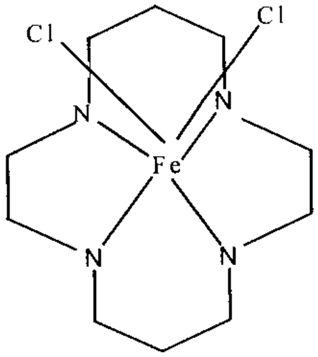
Azamacrocycles generally acts as strong field ligands with the disadvantage that they are usually not able to complete the ion coordination sphere (23). This is the case for iron (III), which is a very hard acidic metal ion. However, this ion has a reasonable affinity for 1,4,8,11-tetraazacyclotetradecane.

Nishida et al.(24,25) suggested that the activity of any complexes towards catalyst in presence of reducing agents, suggesting that an inter mediate should be formed due to lability of the axial chloride ligand (XXI,XXII).



(trans-(Fe(cyclam) Cl2)

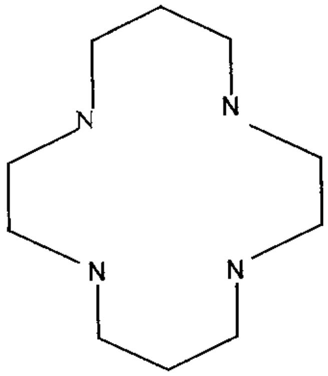
(XXI)



(Cis-(Fe(cyclam) Cl2)

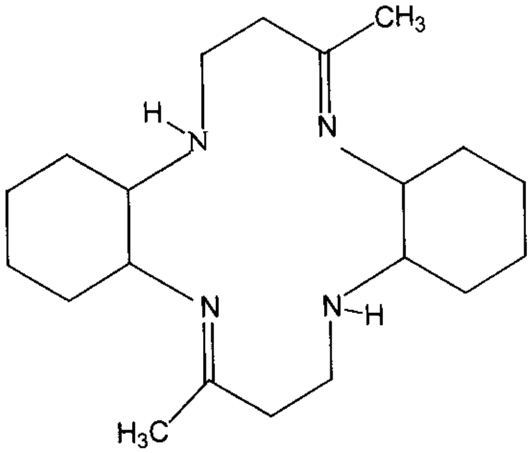
(XXII)

The macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) (XXIII)$^{(26)}$ configuration on a crystallographic center of symmetry, with the electron pairs on 1,8-related N atoms directed away from the center of the ring. Thus, it is not possible from this structure to determine accurately the dimensions of the metal ion binding cavity.

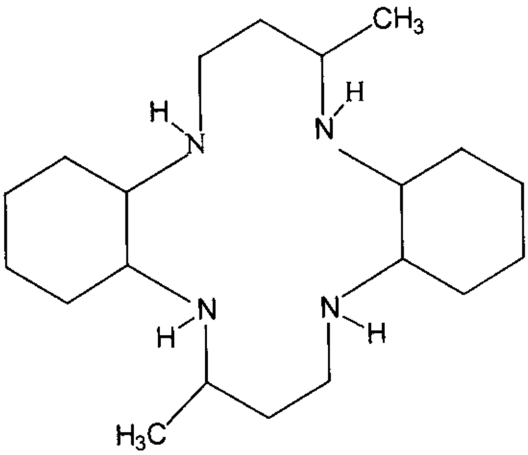


(XXIII)

Tetraazamacrocyclic ligand 3,14-dimethyl-2,6,13,17-tetraaza tricycle(14,4,01.18,07.12)docosa-2,12-diene (XXIV,XXV) that contains two cyclo hexane rings, had been prepared by Geol et al.$^{(27)}$ as its dihydroperchlorate salt. Preparation was done by the non-template condensation of methyl vinyl ketone with 1,2-diaminocyclohexane and perchloric acid produced 3,14-dimethyl-2,6,13,17-tetraazatricyclo (14,4,01.18,07.12)docosane, with square planar Ni(II) and Cu(II) complexes.

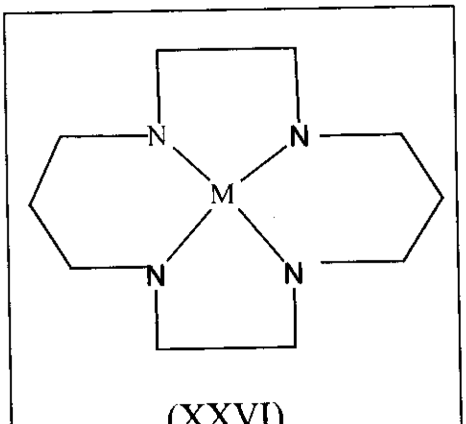


(XXIV)



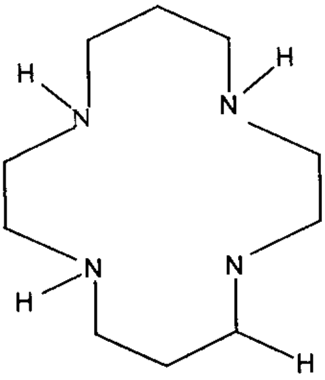
(XXV)

Synthesis and characterization of macrocyclic tetraazacyclotetra decane complexes (XXII) with Cu(II) and Ni(II) were performed by Huey et al.(28). The common features of the macrocyclic compounds were deduced from the relation among the metal ion-nitrogen distances, the chelate angles, the axial lengths, the coordination numbers and many other factors. The hydrogen bonds exist between the ligands and water/anion play an important role to stabilize the crystal structures. The distance between metal and nitrogen expect the structure of the macrocyclic compounds. Ni(II) macrocyclic compounds have six and four coordinations and planar configurations whereas Cu(II) structure have six and five coordinations and planar configurations. There are many factors in the crystal structure determination depending on molecular structure of the ligand and environmental molecule surrounding the ligand, such as water molecules and other anion groups.

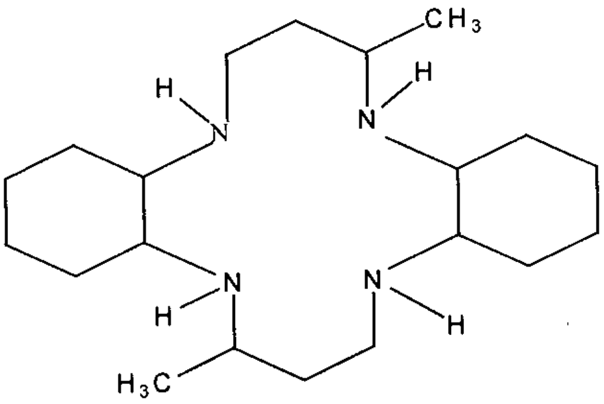


(XXVI)

Cyclam (1,4,8,11-tetraazacyclotetradecane) (XXVI) complexes with Cr(III), Fe(III) and Co(III) were prepared by Kim and Lough$^{(29)}$. The structure and chemical properties appeared to depend on the nature of the central metal ion as well as the structure of the ligand. Substitution on C-or N- on (XXVII- XXVIII) affected the structures and reactivities in avarity of transition metal systems. The addition of substituents on to the ring was generally reflected by loss of ligand flexibility, which is manifested in metal ion complexation behavior that is usually slower relative to (XXVII).



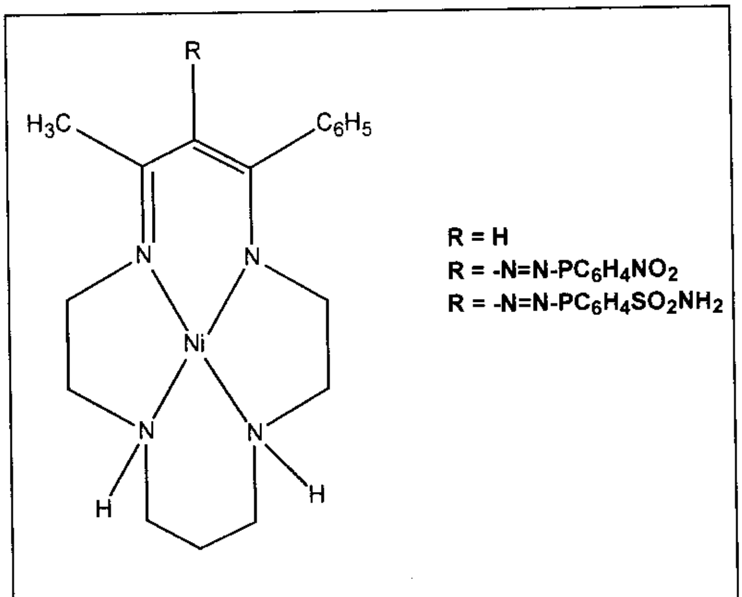
(XXVII)



(XXVIII)

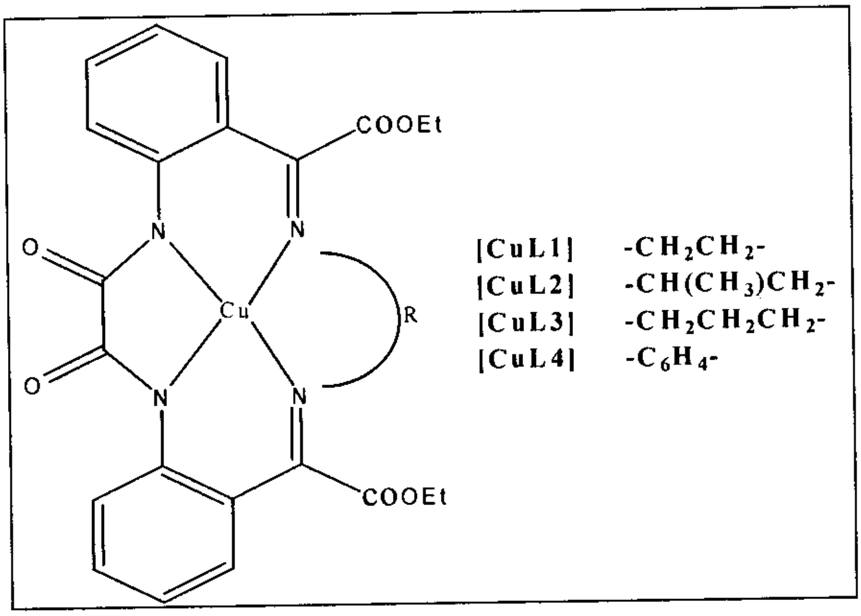
The complexes $[Ni(L_I)(INT)].5H_2O$ and $(L_I)(H_2O)](Cl)(INT).3H_2O$ where L_I(=3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,0 1.18,0 7.12] and INT= isonicotinate were prepared by Youngchoi et al$^{(30)}$. The preparation depended on the reaction of$[Ni(L_I)]Cl_2.2H_2O$, $[Cu(L_I)]Cl_2.2H_2O$ with sodium isonicotinate and heated to reflux for 1h and then cool to room temperature. After standing for few days the product was filtered and recrystallized from a hot water-acetonitrile. The crystal structure for Ni complexes revealed an axially elongated octahedral geometry with two axial isonicotinate ligands (high spin octahedral geometry). For Cu complexes, the coordination environment around the copper atom was a distorted square pyramid with an axial water molecule. The structures of metal complexes with the ligands are affected by several factors, including the metal ion size and ligand topology, such as the cavity size, type and number of donor atoms and sterochemical rigidity.

Synthesis and characterization of some phenyl azo substituted tetraazamacrocyclic complexes of Nickel(II) were reported$^{(31)}$. Electro chemical behavior of the prepared macrocyclic complexes had been examined using polarographic, voltammetric and spectroscopic techniques. These studies showed that both the ligand and the metal are electrochemically active. The electrochemical behavior of the azo function had been shown to occur through a single four-electron process. When a nitro group is also present, the nitro function of the azo moiety was reduced in a six-electron cathodic wave.

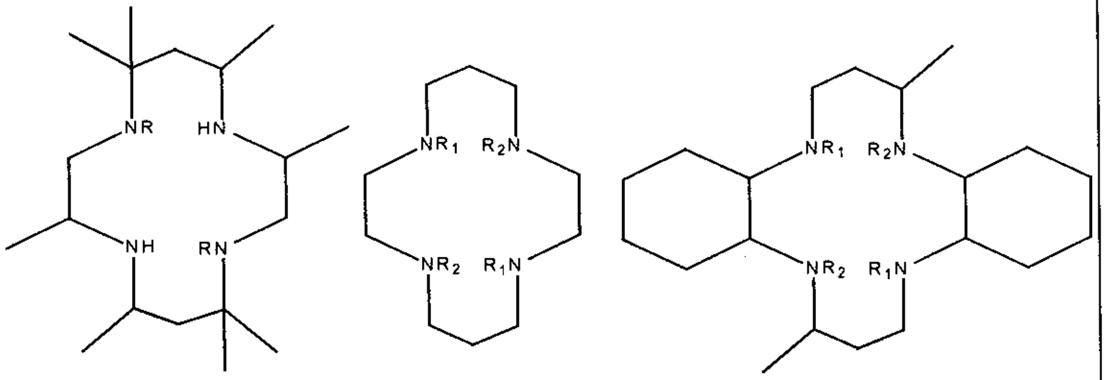


Structure of the Ni(II) complexes

In continuation of their work on magnetism of polynuclear macrocyclic complexes, Gao et al(32-34)described the synthesis, characterization and magnetic properties of the tetranuclear [Cu_3Co] complexes of [14]N_4 and[15]N_4 macrocyclic oxamides. These complexes were of formula [$(CuL^1)_3Co](ClO_4)_2$ (1), [$(CuL^2)_3Co](ClO_4)_2$ (2), [$(CuL^3)_3Co]$-$(ClO_4)_2$ (3) and [$(CuL^4)_3Co](ClO_4)_2$ (4). The structural formula of the mononuclear precursors [(CuL^i] (I =1,2,3,4) is as follows:



New 14-membered tetraaza macrocycles 1,8-diallyl-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (L^2) and 1,8-bis (n-propyl)-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclo tetradecane (L^3) had been prepared by direct reaction of 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (L^1) with alkyl bromide or n-propyl bromide(35). The nickel(II) and copper(II) complexes of L^2 and L^3 had been prepared. The macrocycles showed high copper(II) selectivity against nickel(II) ion in methanol solutions containing water. The wavelengths (505 nm) of the d-d bands for the Ni(II) complexes are extraordinarily longer than those for the complexes of $L^1$and other related di-N-alkylated 14-membered tetraaza macrocycles. Crystal structure of $[NiL^2](ClO_4)_2$ showed that the average Ni-N bond distance (1.992 Å) of the complexes. The effects of the N- and C-substituents on the properties of the macrocyclic compounds were discussed.



L1: R = H
LI: R = $CH_2CH{=}CH_2$
LII:R = $CH_2CH_2CH_3$

L2: $R_1{=}R_2{=}H$
L3: $R_1{=}(CH_2)_3CH_3$; $R_2{=}H$
L4: $R_1{=}R_2{=}CH_3$

L5:$R_1 = R_2 = H$
L6:$R_1 = (CH_2)_2CH_3$; $R_2{=}H$
L7:$R_1{=}R_2{=}CH_3$

A series of electron donors [neutral Ni(II) and Cu(II) complexes of tetraazatetraenemacrocyclic ligands] differing in metal ion, size of the macrocyclic ligand, and the length of the aliphatic bridge linking the macrocyclic units in dimeric species were synthesized and their redox, structural and spectroscopic properties were studied(36). The X-ray results for the donors under study showed a nearly planar geometry of the monomeric tetraazamacrocyclic complexes and interesting "organic-zeolite-like" structures of the dimmers. The dimeric Ni complexes have flexible cavities between the two single ligands linked with aliphatic chains suitable for accommodating some small-sized guests. For the dimeric compounds the metal oxidation [M(II)/M(III)]takes place independently on each center except one binuclear Ni complex, where the cooperativity of the metal centers was observed. Methyl substituents give rise to irreversibility of the oxidation process of the complexes studied. In the absence of these substituents neither reorganization nor ligand addition/elimination kinetics affect the electrode chloranil, tetracyano ethylene and tetracyanoquinodimethane, etc.) was proposed on the basis of their cyclic voltammetric behaviour in the same physicochemical conditions.

The coordinating behaviour of N,N'-bis(1-ethoxycarbonylethyl) ethane-dithioamide (H_2L) was studied by preparing and characterizing the complexes of the types $[M(HL)_2]$, $[M(H_2L)_2]Cl_2$ (M = Pd(II) and Pt(II)) and $[Cu_2(L)X_2]$ (X = Cl and Br)(37). Their structures were studied employing ^{13}C NMR, ESR, IR and UV-VIS spectral methods. In the $[M(HL)_2]$ and $[M(H_2L)_2]Cl_2$ complexes the ligand acts as a bidentate and coordinates through sulfur, giving a square-planar MS_4 surrounding, whereas in the $[Cu_2(L)X_2]$ complexes the ligand acts as a bis(tridentate) with N,S,O-coordination to two copper(II) ions. The electronic and EPR spectra of the $[Cu_2(L)X_2]$ complexes indicated a distorted square-planar symmetry around the Cu(II) ions.

The macrocyclic tetradentate Ni(II) compound was prepared and characterized by X-ray diffraction(38). The crystal structure showed that the molecule is centrosymmetric, and Ni atom located in a square planar

160 °C,10 ppm at 210 °C and 10 ppm at 160 °C, respectively, for the Cu(dmbc)Pc-, Cu(bc)Pc- and MixPc- based gas sensors.

Qin et al. (41) studied the mechanism of catalytic dismutation of superoxide anion by copper(II) complex of 12-(4prime-nitro)-benzyl-1,4,7,10-tetraazacyclotridecane-11,13-d ion was studied by using pulse radiolysis and cyclic voltammetry. The redox potential (E^o) of Cu(II)/Cu(I) was obtained 0.590 V (SCE) in solution of $0.5 mol.dm^{-3}$ Na_2SO_4 . The rate costant (k_{cat}) dismutation was determined to be 1.9×10^6 (pH equals 7.0) and 1.1×10^6 $mol.dm^3.s^{-1}$(pH equals 7.8) by pulse radiolysis and it was suggested that mechanism of catalytic dismutation of O^{2-} is alternate oxidation and reduction of Cu(II) complex by O^{2-}.

Yuming et al. (42) prepared a new macrocyclic heterodinuclear Fe(III) Co(III)complex, by the condensation of 2,6-diformylpyridine N-oxide with 1,3-diaminopropane in the presence of $FeCl_2.4H_2O$ and $CoCl_2.6H_2O$, and formulated as $FeCoLCl_6.C_2H_5OH.8H_2O$.The complexes were characterized by elemental analysis, IR and Mössbauer spectra and investigated electrochemically on an ultramicrodisk platinum electrode. The results showed that the electrode reaction can be thought as a nearly reversible transfer process. The diffusion coefficient is $1.93\times10^{-6}m^2S^{-1}$ and E degree prime is -0.229V (versus s.c.e) and alpha equals 0.877. The average electron transfer rate constant k degree prime is $3.21\times10^{-3}cm\ s^{-1}$.

Two binuclear copper(II) complexes with macrocyclic Schiff bases $Cu_2L_I(CH_3COO)_2.5H_2O$ (complex I) and $Cu_2L_{II}(CH_3COO)_2.2H_2O$(complex II) were synthesized by Dziembowska et al.(43), then characterized by IR,UV, and thermogravimetric analysis (TGA) measurements. TGA was used to investigate the desolvation of lattice water molecules. IR spectra demonstrated the formation of the cyclic compound and together with chemical elemental analysis were used to propose the structure of the complexes. The UV spectra of both complexes were typical for binuclear copper (II) complexes with Robson-type ligands. Variable- temperature magnetic susceptibility measurements corroborated by EPR and low-temperature isothermal magnetization data confirmed the formation of copper dimers with antiferromagnetic exchange coupling constants of -400 and -1250 cm^{-1} for complexes I and II, respectively, residing outside the usual range for the phenoxide bridged Cu(II) complexes. This implies the possibility that additional superexchange paths through the macrocyclic ligand may affect the intradimer exchange interaction as well as the phenoxide oxygen bridges.

The interaction of calf thymus DNA with the copper chelates of 1,10-phenanthroline and tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadec-ane was investigated by Labuda et al(44)at bare and DNA modified glassy carbon electrodes. Modification was affected by immobilizing DNA from a solution containing 5 μg/ml in 10mM-Tris hydrochloride buffer of pH 8 containing 1mM-EDTA; a potential of 0.5 V(vs.SCE) was applied for 120 s. Accumulation of the Cu complex was affected at open circuit conditions for 120 s from a 100micro M solution in 5mM-phosphate buffer of pH 7. After rinsing with water, the electrode was transferred into a blank buffer solution and the cyclic voltammogram was recorded from 0.4 to -0.2 V at 0.1 V/s. Voltammetric data were used for the determination of the bridging constants, binding site size and the ratio of binding constants for the reduced and oxidized forms. A procedure for the detection of DNA cleavage was proposed.

Wanda and Hanna(45), were found that the yttrium and lanthanide perchlorates reacted as templates for the cyclic[1+1] condensation of 2,6-diacetylpyridine with spermine (4,9-diazadodecane-1,12-diamine) to yield

19-membered pentadentate Schiff base macrocyclic complexes with an N_5 set of donor atoms. The complexes were characterized by spectral data (IR,^{1}H NMR, FABMS), thermogravimetric and elemental analysis.

The synthesis and characterization of a Schiff base of p-tert-butylcalix[4]arene(H_2L) and its complex with copper(II) was described$^{(46)}$. The synthesis of H_2L had been achieved by the condensation of salicylaldehyde with the amine group of upper rim monoamine-p-tert-butylcalix[4]arene in ethanol. Attempts for the preparation of metal-ligand (1:2) complexes of this Schiff base with some transition metals failed except for Cu(II), which had been prepared from the copper sulfate, by refluxing in ethanol. The ligand and its complex with copper had been characterized on the basis of elemental analysis and spectral data. Solvatochromisity was observed for the ligand and its copper(II) complex,i.e. in different solvents depending on the solvent polarity, their λ_{max} of absorption in electronic spectra appeared in different wavelengths. Therefore these compounds can be good candidates for nonlinear optical active (NLO) applications. The prepared complex contains two p-tert-butylcalix[4]arene moieties, which could be expect to have improved calixarene ability in the fields like molecular recognition, host-guest features and other calixarene related capabilities.

New transition metal(II) coordination compounds of tetraaza macrocyclic chiral Schiff bases, derived from 2-hydroxybenzlidene acetylacetone or 4-hydroxybenzlideneacetylacetone and (1R,2R)-(-)-1,2-diaminocyclohexane, had been prepared by Srinivasan et al$^{(47)}$. The complexes were characterized spectroscopically and electrochemistry. EPR spectral data for the Cu(II) complexes reveal a strong metal- to- ligand pi-interaction in their square-planar configuration and the broadening of the $g_\perp$ component was due to the strain created by 1R and 2R groups in the cyclohexane rings. The cyclic voltammetric (c.v.) data of the copper complexes show an unusual oxidation state of the Cu^{III} while Co^{II} complexes show a reversible Co^{II}/Co^{III} redox peak along with an additional peak in the negative potential region characteristic of reversibly bound oxygen. The c.v. results revealed that both Cu(II) and Co(II) complexes bind axially with added bases. The spectroscopic results revealed that copper, cobalt and nickel complexes were in square-planar geometry, where as manganese is in octahedral geometry.

Electrochemical stability of eight complexes of the general formula [Co(III)Rdtc(1-8)cyclam]$(ClO_4)_2$, where cyclam = 1,4,8,11-tetrazazcyclo tetradecane and Rdtc(1-8)= 4-morpholine (Morphdtc), 4-thiomorpholine (Timdtc), 4-piperazine (Pzdtc), N-methyl piperazine (N-Mepzdtc), piperidine (Pipdtc), 2-,3-, or 4-methylpiperidine (2-,3- or 4-Mepipdtc) dithiocarbamates, respectively, was studied by Jovanovic et al.(48). The substances were examined in aqueous $NaClO_4$ solution and no aqueous $LiClO_4$ in CH_3CN solution by cyclic voltammetry. In aqueous solution, macrocyclic ligand cyclam was characterized by the anodic peak at 0.95 V. The Rdtc ligands had two anodic peaks, one in the region 0.25-0.30 V and the other in the 0.78-0.95 V region. Absence of these anodic peaks in case of the complexes indicated that coordination to cobalt(III) stabilizes both cyclam and Rdtc ligands, but reversible peaks in the range -0.68 to -0.78 V support the Co(III) redox reaction. In nonaqueous solutions cyclam had one anodic peak at 1.75 V. the ligands with heteroatom in the ring (Morphdtc, Timdtc,Pzdtc, N-Mepzdtc) had two anodic peaks, while the other four ligands (Pipdtc,2-,3- and 4-Mepipdtc) had only one anodic peak. In nonaqueous solution again, coordination to Co(III) ion stabilizes the Rdtc ligands and, unlike in aqueous solution, no Co(III) redox reaction occurs, indicating a greater stability of the complexes in the medium.

The reaction of $[Co(ten)]^{3+}$ (ten=4,4 prime,4 doble prime–ethylidynetris(3-thiabutan-l-amine)) with methanal and base in acetonitrile or water led to the synthesis of an unusual pendant-arm macrocyclic complex,8-(4prime–ammonio-2prime–thiabutyl)-8-methyl-1-oxa-6,10-di thia-3,13-diazacyclo-tetradecane(chloro)cobalt(III)triperchlorate trihdrate(49). The structure of the complex had been established by X-ray crystallographic analysis and such molecules can readily be tied to polymers and proteins. The synthesis, chemical reaction, spectroscopy and electrochemical properties of the macrocyclic complex were described.

Three new cationic mixed-ligand Cu(II) complexes with N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetra azacyclo tetra decane(tpmc) and bridging aromatic mono-or dicarboxylate ligands were prepared by Vuckovic et al.(50). Elemental analysis, conductometric and magnetic measurements, as well as electronic and IR spectroscopy were employed for their characterization. It was proposed that the complexes $[Cu_2(C_6H_5COO)tpmc](CLO_4)_3MeOH$ and $[Cu_2(Hpht)tpmc](ClO_4)$. $3H_2O(H_2pht=$ phthalic acid) were binuclear with μ-coordination of the carboxylate monoanions. The third complex, $[Cu_4ipht(tpmc)_2]$ $(ClO_4)_6NaClO_42MeCN(H_2ipht=$isophthalic acid) was one of the rare tetranuclear Cu(II)-tpmc complexes with an aromatic dicarboxlate ion bridging two Cu_2tpmc units. This was also confirmed by preliminary results of the determination of the crystal structure.

A dinuclear copper(II)$[(LCu)(MeOH)Cu(phen)(MeOH)]ClO_4.NO_3$ macrocyclic complex (where H_2L = 2,3-dioxo-5,6:15,16-dibenzo-1,4,8,13-tetraazacyclo-pendadeca-7,13-diene;phen=1,10-phenanthroline) had been synthesized by Shi-Bin et al.(51). The complexes were characterized by means of elemental analysis and their IR spectrum. The crystal structure had been determined by single-crystal X-ray diffraction. In the complex, both the copper ions were penta-coordinate and had a distorted square pyramid configuration. Magnetic susceptibility measurements show antiferro-magnetic exchange interactions ($J=-207.64\ cm^{-1}$) between the copper(II) ions.

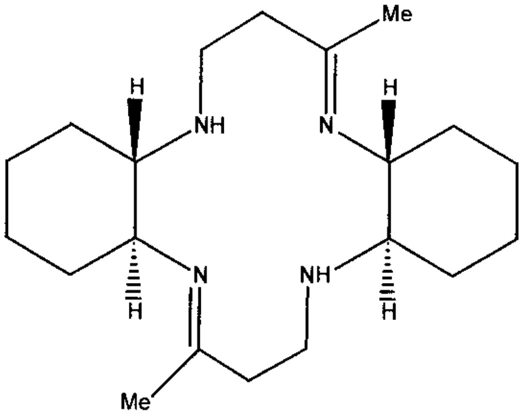
A novel trinuclear complex, $[Co(NiL)_2(H_2O)_2](ClO_4)_2.2C_2H_5OH$, was prepared by self-assemebly using [NiL] as a new complex ligand$^{(52)}$ L is dianion of dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxodibenzo] tetraazacyclotetradecine-13,18-dicarboxylate. The structure of the trinuclear complex was determined by X-ray crystallographic. The Co^{II} ion was at the center of the trinuclear complex cation and occupies a distorted octahedral O_6 environment, approximating to O_h with a^4T_{1g} ground state for Co^{II} that has an unquenched spin-orbit coupling reflected in the magnetic properties. Two Ni^{II} ions reside in completely same and slightly distorted square-planar N_4 coordination geometries. Co^{II} and each Ni^{II} were bridged by an oxamido group from one of the two macrocyclic ligands (L).

O-H Midline ellipsis O and pi Midline ellipsis pi interactions link the trinuclear fragments, perchlorate ions and C_2H_5OH molecules to form three dimensional superamolecular architecture.

The crystal structures of (2,6-dioxo-1,4,7,11,14-pentaazacyclo-heptadecanato)copper(II)tetrahydrate, $[Cu(C_{12}H_{23}N_5O_2)].4H_2O$,(I), (3,16-dioxo-1-oxa-4,8,11,15-tetraazacycloheptadecanato)copper(II)pentahydrate, $[Cu(C_{12}H_{22}N_4O_3)].5H_2O$,(II), and (3,16-dioxo-1-thia-4,8,11,15-tetraaza cycloheptadecanato)copper(II)trihydrate $[Cu(C_{12}H_{22}N_4O_2S)].3H_2O$, (III), were reported by Gerrite et al. $^{(53)}$. The coordination geometry in each case was approximately square pyramidal with two amino groups and two deprotonated amide groups in the basal plane. The apical position is occupied by an amine group, an ether O atom or a thio S atom. Trigonal distortion increased in the sequence S less than O less than N as apical donor. The relation between the distortion in the basal plane of the complexes and the maxima in their electronic spectra was discussed.

Unpyrolzed transition-metal macrocyclic complexes were examined by Andrew and Jerry(54) for possible use in polymer electrolyte fuel cells (PEFC). Test results showed that cobalt complexes generate more H_2O_2 than iron complexes in oxygen reduction. Cobalt complexes were more stable than iron complexes in an acid electrolyte when bound with Nafion registered trademark but high peroxide yields during oxygen reduction make them unsuitable for practical use.

Goal and Jeong(55) had considerable interest in the preparation of various types of C- and/or N-configurational isomers of polyaza macro cyclic complexes. In particular, 14-membered macrocyclic complexes having one or two 1,2-diaminocyclohexane subunit(s) theoretically occur as various C- configurational isomers because the diamino cyclo hexane subunit exists as either cis- or trans –isomer. Although both $[Ni(3t)](ClO_4)_2$ and $[Ni(3c)](ClO_4)_2$ have a square-planar coordination geometry, which (chart 1) indicate that their chemical properties and stereochemistry vary with the isomeric structure of the 1,2-diaminocyclohexane subunit. Furthermore, the chemical properties of $[Ni(4a)]^{2+}$, even though both of them contain cis-1,2-diaminocyclohexane subunits. C-methylated complexes, $[Ni(1t)]^{2+}$ and $[Ni(2t)]^{2+}$, containing two trans-1,2-diamino cyclohexane subunits had been also reported by Geol(26,56,57). They prepared the nickel(II) complexes of 1c and 2c, having two cis-1,2-diaminocyclohexane subunits. It was found that the axial coordination of a solvent molecule, such as methyl cyanide(MeCN) or Dimethyl formamide (DMF), is much easier to $[Ni(2c)]^{2+}$ than to$[Ni(2t)]^{2+}$. The coordination behavior of $[Ni(2c)]^{2+}$is also considerably different from that of $[Ni(3c)]^{2+}$ by comparing the structure and chemical properties of $[Ni(1t)]^{2+}(ClO_4)_2$ with those of $[Ni(2t)]^{2+}$, $[Ni(3c)]^{2+}$, and other related nickel(II) complexes.



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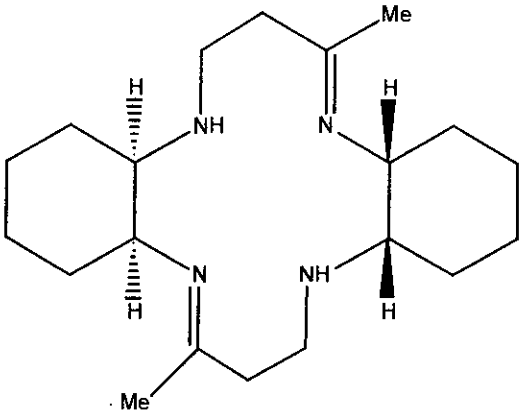
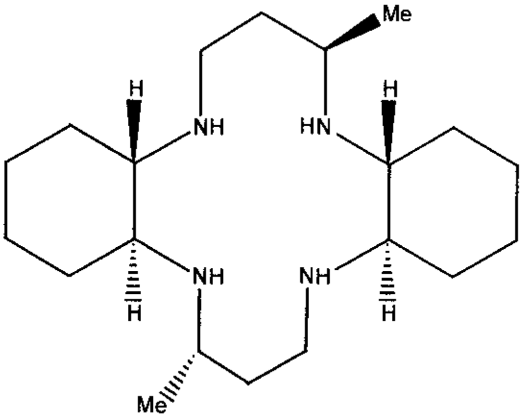
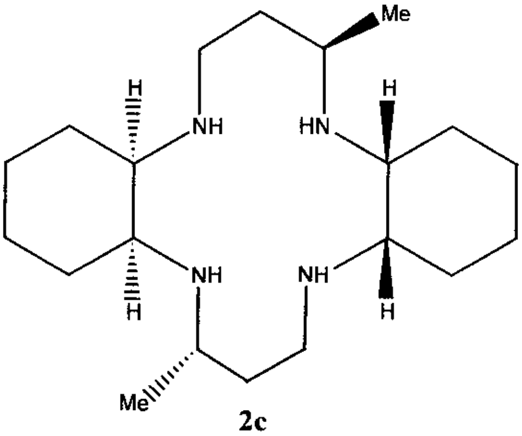


1c



2t



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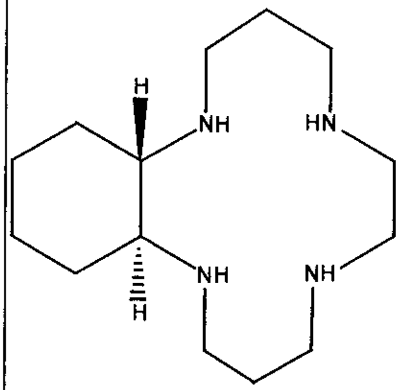

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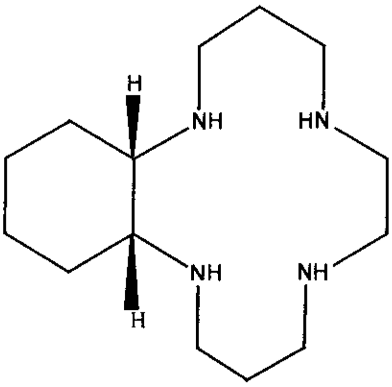

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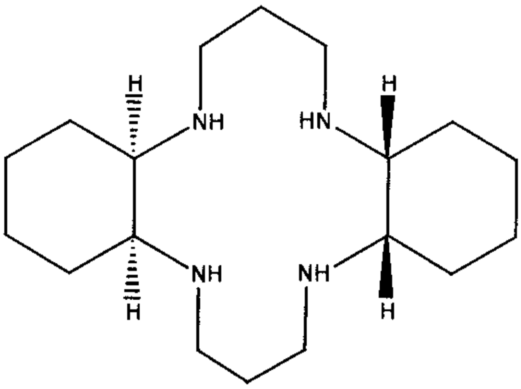
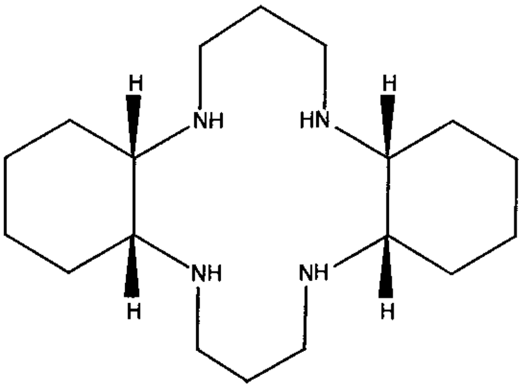


4a

Chart 1



4s